

CLAIMS

WHAT IS CLAIMED IS:

1. A method for solid free-form fabrication of a three-dimensional object, comprising:
 - depositing a particulate blend in a defined region, said particulate blend including radical source particulates, polyacid particulates, multivalent cation particulates, and calcium phosphate source particulates;
 - ink-jetting a liquid phase binder onto a predetermined area of said particulate blend to form hydrated cement in said predetermined area, wherein said liquid phase binder is acidic and includes reactive monomers; and
 - setting said hydrated cement.
2. The method of claim 1, further comprising removing a portion of said particulate blend that does not form said hydrated cement.
3. The method of claim 1, wherein said setting said hydrated cement further comprises:
 - performing a polymerization setting reaction;
 - performing an acid/base setting reaction; and
 - performing a re-precipitation setting reaction.
4. The method of claim 1, wherein said reactive monomers comprise one of 2-hydroxyethylmethacrylate or 2-hydroxybutylmethacrylate.
5. The method of claim 1, wherein said radical source particulates comprise one of benzophenone or an ultraviolet/blue light initiator.
6. The method of claim 5, further comprising radiating said hydrated cement with ultraviolet light.

7. The method of claim 1, wherein said polyacid particulates comprise one of polyacrylic acid (PAA), polyvinyl pyrrolidone-co-maleic acid, or polyethylene-co-methacrylic acid.

8. The method of claim 1, wherein said multivalent cation particulates comprise one of calcium (2+) or aluminum (3+).

9. The method of claim 1, wherein said calcium phosphate source particulates comprises one of mono-calcium phosphate, di-calcium phosphate, tri-calcium phosphate, or tetra-calcium phosphate.

10. The method of claim 1, wherein said liquid phase binder further comprises one of phytic acid, itaconic acid, diglycolic acid, or phosphoric acid.

11. The method of claim 1, wherein said liquid phase binder further comprises multifunctional monomers including glycol dimethacrylate.

12. The method of claim 1, wherein said particulate blend further comprises reaction accelerators.

13. The method of claim 12, wherein said reaction accelerators comprise one of tartaric acid, citric acid, glutamic acid, diglycolic acid, DL aspartic acid, iminodiacetic acid, itaconic acid, or $\text{NH}_4\text{H}_2\text{PO}_4$.

14. The method of claim 1, wherein said particulate blend further comprises strengthening agents.

15. The method of claim 14, wherein said strengthening agents comprise nanocomposites.

16. The method of claim 15, wherein said nanocomposites comprise one of PEO/clay nanocomposites, hydroxyapatite nanocomposites, layered double hydroxide (LDH) nanocomposites, or organophilic nanocomposites.

17. The method of claim 1, wherein said liquid phase binder comprises colorants.

18. The method of claim 1, wherein said aqueous binder comprises water, organic acid, water soluble acrylic monomers, mineral acid, catalyst, dye colorants, pigment colorants, pyrrolidone, 1,5-hexanediol, liponic ethylene glycol, and surfynol 465.

19. A system for solid freeform fabrication of three-dimensional objects comprising:

a particulate blend including polyacid particulates, multivalent cation particulates, and calcium phosphate source particulates;

a radical forming source; and

an acidic ink-jettable aqueous binder including reactive monomers and multifunctional monomers, wherein said ink-jettable aqueous binder is configured to hydrate said particulate blend to form a cement.

20. The system of claim 19, wherein said radical forming source is disposed in said particulate blend.

21. The system of claim 19, wherein said radical forming source is disposed in said aqueous binder.

22. The system of claim 19, wherein said radical source particulates comprise one of benzophenone or an ultraviolet/blue light initiator.

23. The system of claim 22, wherein radiating said hydrated cement with ultraviolet light initiates a polymerization reaction.

24. The system of claim 19, wherein said reactive monomers comprise one of 2-hydroxyethylmethacrylate or 2-hydroxybutylmethacrylate.

25. The system of claim 19, wherein said polyacid particulates comprise one of polyacrylic acid (PAA), polyvinyl pyrrolidone-co-maleic acid, or polyethylene-co-methacrylic acid.

26. The system of claim 19, wherein said multivalent cation particulates comprise one of calcium (2+) or aluminum (3+).

27. The system of claim 19, wherein said calcium phosphate source particulates comprises one of mono-calcium phosphate, di-calcium phosphate, tri-calcium phosphate, or tetra-calcium phosphate.

28. The system of claim 19, wherein said liquid phase binder further comprises one of phytic acid, itaconic acid, diglycolic acid, or phosphoric acid.

29. The system of claim 19, wherein said multifunctional monomers comprise glycol dimethacrylate.

30. The system of claim 19, wherein said particulate blend further comprises reaction accelerators.

31. The system of claim 30, wherein said reaction accelerators comprise one of tartaric acid, citric acid, glutamic acid, diglycolic acid, DL aspartic acid, iminodiacetic acid, itaconic acid, or $\text{NH}_4\text{H}_2\text{PO}_4$.

32. The system of claim 19, wherein said particulate blend further comprises strengthening agents.

33. The system of claim 32, wherein said strengthening agents comprise nanocomposites.

34. The system of claim 33, wherein said nanocomposites comprise one of PEO/clay nanocomposites, hydroxyapatite nanocomposites, layered double hydroxide (LDH) nanocomposites, or organophilic nanocomposites.

35. The system of claim 19, wherein said liquid phase binder comprises colorants.

36. The system of claim 19, wherein said aqueous binder further comprises a co-initiator.

37. The system of claim 19, wherein said particulate blend further comprises a co-initiator.

38. The system of claim 19, wherein said aqueous binder comprises water, organic acid, water soluble acrylic monomers, mineral acid, catalyst, dye colorants, pigment colorants, pyrrolidone, 1,5-hexanediol, LEG, and surfynol 465.

39. The system of claim 19, further comprising an ink-jet material dispenser configured to selectively jet said ink-jettable aqueous binder onto said particulate blend.

40. The system of claim 19, further comprising a substrate configured to carry said particulate blend in a defined region, said defined region being configured with respect to said ink-jet material dispenser such that said ink-

jettable aqueous binder, upon being ink-jetted from said ink-jet material dispenser, contacts said particulate blend.

41. The system of claim 19, wherein said system is configured to apply multiple layers of cement such that each layer of said cement is bound to at least one adjacent layer.

42. The system of claim 19, wherein said particulate blend comprises tricalcium phosphate, tetracalcium phosphate, hydroxyapatite, polyacrylic acid, polyethylene-co-methacrylic acid, polyvinyl pyrrolidone-co-maleic acid, citric acid, ascorbic acid, $\text{Cu}(\text{NO}_3)_2$, benzophenone, and layered double hydroxide nanocomposites.

43. The system of claim 19, wherein said cement sets due to a polymerization setting reaction, an acid/base setting reaction, and a re-precipitation setting reaction.

44. The system of claim 19, wherein said ink-jettable aqueous binder comprises components configured to improve jettability of said ink-jettable aqueous binder, said components including water and surfactants.

45. A solid three-dimensional prototype composition, comprising:
multiple layers of cement deposited in contact with one another, each of said multiple layers of cement comprising a particulate blend including radical source particulates, polyacid particulates, multivalent cation particulates, and calcium phosphate source particulates;

wherein said particulate blend was hydrated and hardened by use of an ink-jettable aqueous binder.

46. The composition of claim 45, wherein said ink-jettable aqueous binder comprises:

an acid;
reactive monomers; and
multifunctional monomers.

47. The composition of claim 45, wherein said multiple layers of cement further comprises reaction accelerators.

48. The composition of claim 45, wherein said multiple layers of cement further comprises strengthening agents.

49. The composition of claim 48, wherein said strengthening agents comprise nanocomposites.

50. The composition of claim 45, wherein said multiple layers of cement further comprises a colorant.

51. The composition of claim 50, wherein said composition was set as a result of a polymerization setting reaction, an acid/base setting reaction, and a re-precipitation setting reaction.